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The Promoter Action of Thoria on Nickel Catalysts

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THE PROMOTER ACTION OF THORIA ON NICKEL CATALYSTS

BY WILLIAM WALKER RUSSELL

In view of some recent work[1] in the field of promoter action, it was deemed of importance to obtain information regarding the adsorptive capacities of promoted nickel catalysts for gases reacting at their surfaces. The promoting action of several irreducible oxides on nickel used to catalyze the methanation reaction between carbon monoxide or carbon dioxide and hydrogen has been demonstrated by Medsforth. This author believes that the function of the promoter is to dehydrate the unstable intermediate compound formed in the above reactions, and that, in general, promoters act selectively: (a) to decompose intermediate compounds formed by the catalyst, (b) to form intermediate compounds which are decomposed by the catalyst, (c) to adsorb or combine with one of the reacting substances thereby increasing its concentration on the catalyst. Armstrong and Hilditch, in a study of the hydrogenation of oils in the presence of nickel and nickel plus various irreducible oxides, conclude that the main source of promoter action is a mechanical one, and that it involves simply an increase of the available surface of the nickel. It is of interest to note that alumina which was used as a promoter for supported nickel by each of these authors exerted its maximum effect at approximately the same concentration in each of the two types of reaction studied.

The present investigation, which has been confined to a study of the promoting action of thoria on nickel used to catalyze the interaction of carbon dioxide and hydrogen to form methane and water, was attempted in the hope of somewhat further elucidating the mechanism of promoter action. It is clear that if the function of the promoter is simply to increase the available surface of the catalyst, an increase in catalytic activity due to the presence of a promoter, as shown by reaction velocity measurements, must be accompanied by a corresponding increase in adsorptive capacity. If such a corresponding increase in adsorptive capacity is not found, it is strong evidence for a qualitative rather than a quantitative change in the surface of the catalyst. The experimental work, especially that on supported catalysts, presented in this paper shows that no proportionate increase in adsorption accompanies the increase in activity shown by the promoted catalyst. It appears, therefore, that the promoted catalyst has a much more active surface. Further discussion of this point will be reserved until the evidence is presented.

On account of the known difficulty in reproducing catalysts of desired properties it was considered essential to make both adsorption and reaction velocity measurements on the same sample of catalyst. A method has been devised for doing this, and the same procedure has been followed both for the supported and for the unsupported catalysts.

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[1] Medsforth: J. Chem. Soc., **123**, 1452 (1923); Armstrong and Hilditch: Proc. Roy. Soc., **103** A, 586 (1923).

Experimental

Apparatus.—The apparatus used for the reduction of the catalysts and for the reaction velocity measurements is shown in Figs. 1 and 2. The catalyst tube is seen to be divided into two portions by a constriction. The proper amount of the unreduced oxide was placed in A, Fig. 1, and then a bit of glass wool placed in the lower part of B, which was then filled with a quantity of the same oxide sufficient to give the amounts of catalyst desired for reaction velocity measurements. The constriction was thus kept free from oxide. The thermometer C, was placed well down in the catalyst mass in B and the connection at D was made tight with a piece of rubber tubing. During reduction,

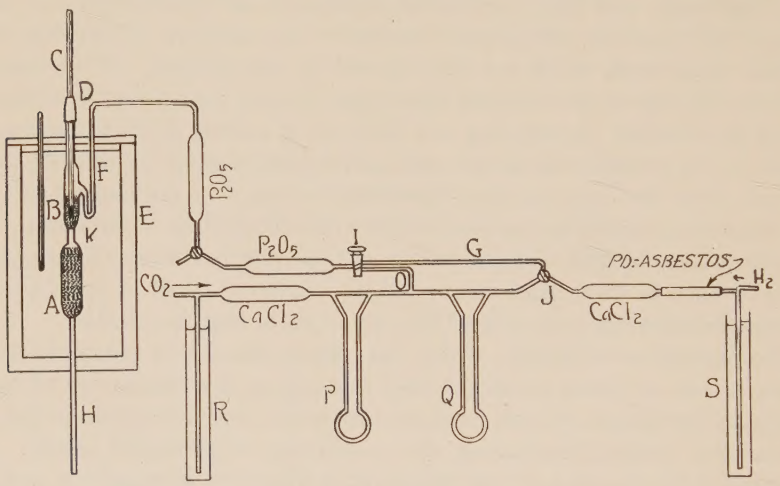

FIG. 1

the catalyst tube was heated by means of the large furnace E, which was wound with nichrome wire. Hydrogen for reduction was led through the by-pass G, thence through the phosphorus pentoxide tubes and the preheater F, and into the catalyst tube. The effluent hydrogen and water vapor passed out at H through a sulphuric acid trap. When reduction was complete, as shown by weighings of a phosphorus pentoxide tube through which the effluent hydrogen could be passed, the furnace was cooled to room temperature. The hydrogen was replaced by carbon dioxide which could be led into the system through tap I., the three-way tap J being closed. Meanwhile the furnace H was removed, so that the catalyst tube was held suspended only by the furnace cover. The tube A was removed by sealing off at K and quickly sealed in place on the adsorption apparatus by means of the capillary tube H. Keeping the catalyst in B under a positive pressure of carbon dioxide, a short piece of glass tubing was sealed on at K the pressure of the carbon dioxide being used in making the seal. During this operation the tube B was swung into a horizontal position to prevent heating the catalyst mass. Fig. 2 shows the changes made in the furnace in order to make the reaction velocity measure-

ments. A shorter furnace L was substituted for E after sealing on the tube M. A small furnace N, which could be raised and lowered, was placed around M to prevent any water from condensing along this tube.

Reaction Velocity Measurements.—In the experiments on reaction velocity, the two interacting gases, carbon dioxide and hydrogen came in contact at O (Fig. 1) and then passed through the two phosphorus pentoxide tubes where they were thoroughly dried and mixed before entering the preheater F and catalyst tube B. The amount of carbon dioxide in the mixture could be controlled by the flow meter P, and the amount of hydrogen by means of its flow meter Q. The traps R and S which contained water served for the regulation of the pressures of the two gases. As shown in Fig. 2, the exit gases were passed through the phosphorus pentoxide weighing tube and then through a sulphuric acid trap to the air. In making a run, hydrogen alone was passed over the catalyst, while the temperature was raised to the maximum to be reached during the run, until weighings of the phosphorus pentoxide tube showed that no water was being evolved. The temperature was then adjusted somewhat below that desired for the first measurements, and carbon dioxide was allowed to enter the system. During all runs, the gas mixture was kept at a ratio of 6 to 1 for hydrogen to carbon dioxide. When the gas mixture was correctly adjusted and the temperature regulated, the reaction was allowed to proceed an hour or more, to insure steady conditions, before measurements were made. During this time the exit gases passed directly from the catalyst tube to the acid trap. Measurements were made by interposing a weighed phosphorus pentoxide tube for 15 minutes, the gain in weight due to the water formed in the reaction being then determined. Determinations were made at a given temperature until several checks were obtained, showing that a steady condition existed. During the periods when the catalyst was not in use, it was maintained at room temperature under a positive pressure of hydrogen. The flow meters were calibrated with the gas with which they were to be used and under the conditions of experiment, the gases being collected and measured over mercury. These meters were frequently checked between runs. Also, during runs, the correctness of the carbon dioxide flow meter could be checked by raising the temperature so as to secure 100% conversion.

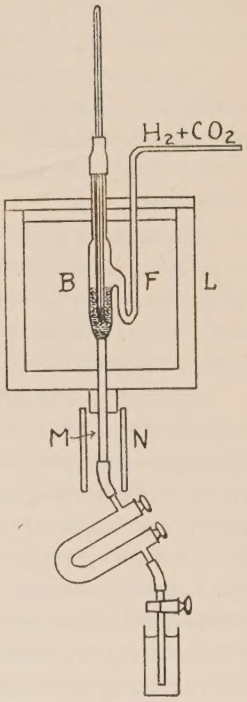

FIG. 2

Adsorption Measurements.—The apparatus used and the technique employed in adsorption was essentially that developed in the Princeton laboratories.[1] All measurements were made at or near atmospheric pressure

[1] See Pease: J. Am. Chem. Soc., **45**, 1197 (1923).

and over a range of temperatures. Temperatures were maintained as follows: 0° with crushed ice and water, 110° with toluene vapor, 218° with naphthalene vapor, and 285° and 345° with an electrically heated air bath.

Preparation and Purification of Gases.—The gases were prepared and purified in the same manner for both the reaction velocity and the adsorption measurements.

Electrolytic hydrogen was passed over heated palladized asbestos, to remove oxygen, and dried over phosphorus pentoxide.

Carbon dioxide was generated in a Kipp generator by the interaction of dilute hydrochloric acid and marble, passed through a solution of sodium bicarbonate, and finally dried over phosphorus pentoxide.

Compressed nitrogen containing only a slight amount of oxygen was purified by passage through ammonium cuprous carbonate solution, washed with dilute sulphuric acid, then with concentrated sodium hydroxide solution, passed over red-hot copper turnings, and finally dried over phosphorus pentoxide.

Preparation of Catalysts.—Pumice ground to 20-40 mesh was used as a supporting material. It was purified by boiling with aqua regia until free from iron. It was then washed free from chlorides and nitrates, dried on a water bath, and finally over a free flame to dusty dryness. It was kept in a tightly stoppered bottle.

Catalyst I was prepared by allowing 16 grams of the prepared pumice, volume 52.44 ccs., to absorb uniformly 10 ccs. of standard nickel nitrate solution equivalent to 1.6 grams of metallic nickel. The standard nickel nitrate solution was made by dissolving 79.29 grams of pure nickel nitrate in water, making up the total volume to 100 ccs. The impregnated pumice was dried for two hours on the water bath. One sixteenth of the total weight of this material, corresponding to one tenth gram of nickel on one gram of pumice, was separated for reaction velocity measurements. The remainder was placed in the lower part of the catalyst tube for use in adsorption measurements while the portion separated was placed in the upper part of the tube and the whole arranged for reduction as previously described. The temperature of the furnace was slowly raised to 200°, during a period of three hours while dry air was sucked through, then more rapidly to 350° and kept there until no more oxides of nitrogen were evolved. The furnace was allowed to cool and the air displaced by hydrogen. The temperature was then raised to 350° and reduction continued at this temperature until less than 1 milligram of water formed per hour as determined by weighing a phosphorus pentoxide tube through which the exit hydrogen passed. The time of reduction was 228 hours. The catalyst was dull black in appearance. Catalyst II was identical in every way with Catalyst I except that it contained in addition 0.16 grams of thoria. The thoria was incorporated by dissolving 0.3338 grams of pure thorium nitrate (this nitrate on analysis had been found to contain 47.93% ThO_2) in the 10 ccs. of the standard nickel nitrate solution used to impregnate the pumice. Reduction at 350° was continued, as with Catalyst I, until less

than 1 milligram of water formed per hour. The time of reduction was here, also, 228 hours. This catalyst had a jet-black color.

Catalyst III was unsupported nickel. It was prepared by calcination of pure nickel nitrate to form nickel oxide, which was subsequently reduced in the same apparatus and in the same manner as the supported catalysts. The temperature of reduction was 250°. It required 192 hours to reduce this catalyst to the point where less than 1 milligram of water formed per hour. The catalyst was a dull black, rather dense powder.

Catalyst IV was also unsupported nickel but contained 2% ThO_2 calculated upon the weight of nickel present in the nickel nitrate used. It was prepared by heating nickel nitrate until it dissolved in its water of crystallization and then dissolving the required amount of thorium nitrate in this melt. After thorough mixing, the temperature was raised slowly until oxides of nitrogen were evolved, and calcination was allowed to proceed as in the preparation of Catalyst III. This catalyst was prepared for reaction velocity measurements only. The temperature of reduction was 250° and the time 192 hours. This catalyst was a jet-black powder.

Catalyst V was unsupported nickel and contained 10% thoria calculated upon the weight of nickel. The thoria was incorporated as in Catalyst IV and reduction was carried out as with Catalyst III. The temperature of reduction was 250° but it was necessary to continue reduction for 384 hours before the water content of the effluent hydrogen fell to 1 milligram per hour. This catalyst was a rather light powder of jet-black color.

Heat treatment.—The unsupported catalysts were subjected to a standard heat treatment. The identical treatment was given to catalysts intended for adsorption measurements as was given to catalysts intended for reaction velocity work. It consisted in heating the catalyst in an atmosphere of hydrogen for 1 hour at 400°, the temperature being raised to 400° and lowered again at a given rate. Some reduction occurred during this treatment but it was of slight import as compared to the effect produced by sintering. It was not possible to heat the catalyst in the reaction velocity tube in vacuo, and perhaps it would not have been altogether desirable to heat the catalyst bulb in the adsorption apparatus for any length of time at 400° when evacuated, because of the slow deformation of the glass bulb which might occur.

Supported Catalysts

Adsorption Measurements on Supported Catalysts:—The adsorptive capacities of Catalysts I and II for the reacting gases and nitrogen are shown in Table I. These two catalysts were identical in every way except that II contained 10% thoria.

Both catalysts show a large adsorption of nitrogen at 0°, intermediate between that of hydrogen and that of carbon dioxide. The pumice support is responsible for this large adsorption of both carbon dioxide and nitrogen at this temperature. In the case of the former gas it would seem probable that liquefaction has occurred in the capillaries but in the case of nitrogen the

TABLE I

Adsorption on Catalyst I

Wt. nickel = 1.500 gms; Wt. pumice = 15.000 gms; Apparent vol. = 49.16 cc.

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.					Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.				
	0°	110°	218°	285°	345°	0°	110°	128°	285°	345°
N_2	68.5	37.55	28.2	24.45	21.9	18.9	2.2	.65	.2	0
H_2	55.4	41.05	32.45	28.8		5.8	5.7	4.9	4.5	
CO_2		76.05	34.7	27.65	23.75		40.7	7.15	3.4	1.85

Adsorptions on Catalyst II

Wt. nickel = 1.500 gms; Wt. thoria = 0.1500 gms; Wt. pumice = 15.00 gms.
Apparent vol. = 49.16 cc.

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.					Vol. gas N. T. P. adsorbed by sample at t°, 760 mm.				
	0°	110°	218°	285°	345°	0°	110°	218°	285°	345°
N_2	69.8	38.25	28.8	25.2	22.6	18.65	1.8	.35	.1	0
H_2	57.75	42.95	34.25	30.55		6.6	6.5	5.8	5.45	
CO_2	407.9	78.15	36.25	29.35	25.25	356.8	41.7	7.8	4.3	2.65

Comparison of Adsorptions on Catalysts I and II

Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.

Catalyst	Gas	0°	110°	218°	285°	345°
II	H_2	6.6	6.5	5.8	5.45	
I	H_2	5.8	5.7	4.9	4.50	
Increase		.8	.8	.9	.95	
Percentage increase		13.8	14.04	18.37	21.1	
II	CO_2		41.7	7.8	4.3	2.65
I	CO_2		40.7	7.15	3.4	1.85
Increase			1.0	.65	.90	.80
Percentage increase			2.46	9.09	26.47	43.24
II Ratio	$\frac{CO_2}{H_2}$		6.4	1.3	.8	
I Ratio			7.1	1.5	.8	

temperature is far above that of the critical temperature (−146°C) of this gas[1]. Previous work in the Princeton laboratories has shown no appreciable adsorption of nitrogen when diatomite brick was used as a support, and little or none has apparently occurred with unsupported nickel catalysts dealt with later in this paper.

In calculating the amounts of the gases adsorbed, it has been assumed that the nitrogen adsorption occurring at 345°, the highest temperature at which measurements were made, was negligible. This assumption gives values for nitrogen adsorption at 285° which are very small e.g. 0.1 and 0.2 cc., and for the comparative purposes for which these adsorption values are useful can involve no appreciable error.

The hydrogen adsorption on either catalyst shows comparatively little change with temperature as has been previously observed in the case of supported nickel alone[2]. The promoted catalyst shows an increased adsorption

[1] Landolt-Börnstein-Roth-Scheel.

[2] Gauger and Taylor: J. Am. Chem. Soc., **45**, 920 (1923).

at all temperatures investigated. The actual increase varies from 0.8 to 0.95 cc. over the range 0°—285°. The percentage gain in hydrogen adsorption of the promoted catalyst over the unpromoted in the range 110°–285° shows a linear increase with temperature. This is shown graphically in Fig. 3.

The carbon dioxide adsorptions at 0° are doubtless largely due to liquefaction, a value of 356 ccs. having been obtained at 0° for this gas on Catalyst II. Even at 110° adsorption is also without doubt largely of the secondary or unreactive type. At all temperatures, however, the promoted catalyst shows the greater adsorptive capacity. The actual increase in carbon dioxide adsorption which Catalyst II shows over Catalyst I varies from 0.65 to 1.0 cc. in th. range 0°—345°. As may be seen in Fig. 3, the percentage increase in the ase sorption of this gas becomes nearly linear in the temperature range 220°–345°-

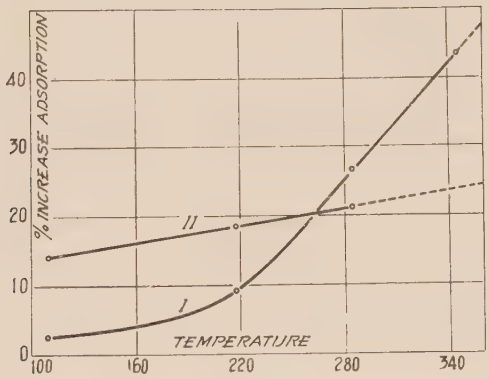

FIG. 3

The percentage increases in adsorption shown by Catalyst II over Catalyst I. Curve I-hydrogen. Curve II-carbon dioxide.

The nitrogen adsorptions are somewhat less on the promoted catalyst. This may be due, as Armstrong and Hilditch suggest, to the plugging of some of the pores of the pumice support by the thoria.

Reaction Velocity Measurements on Supported Catalysts.—The activities of Catalyst I and II, as shown by their capacities for catalyzing the interaction of hydrogen with carbon dioxide, are shown graphically in Fig. 4. Temperature has been plotted horizontally and percentage conversion vertically. The same amount of each catalyst was used, and conditions of experiment were identical for both, so that the results should be completely comparable. With both catalysts, the rate of reaction increases linearly with the temperature at rates of conversion between 20 and 75%. Curve 1 in Fig 4 shows the steady behavior of Catalyst I, and curve 2 that of Catalyst II, both at the same rate of flow, 35 ccs. per minute. The promoted catalyst shows the same activity 55°–60° lower than the unpromoted one.[1] The temperature coefficient of the

[1] In this connection it is interesting to note that adsorption measurements of hydrogen on Catalyst II when it already held some adsorbed carbon dioxide showed that these two gases interacted even at 110°C., although very slowly.

reaction on the more active catalyst appears somewhat greater when rates of flow are the same for both catalysts. When, however, the rate of flow on Catalyst II is increased until its rate of conversion is practically the same as for Catalyst I at a flow rate of 35 cc. per minute, the temperature coefficients become the same. The slope of curve 3, which shows the behavior of Catalyst I at a rate of flow of 49 ccs. per minute after the catalyst had been somewhat deactivated by allowing the reaction to proceed at 400°, indicates that the reaction now has a somewhat smaller temperature coefficient. It may be noted here, and it will be shown more strikingly in the case of unsupported nickel catalysts, that the more active the catalyst the greater the temperature coefficient of the reaction catalyzed.

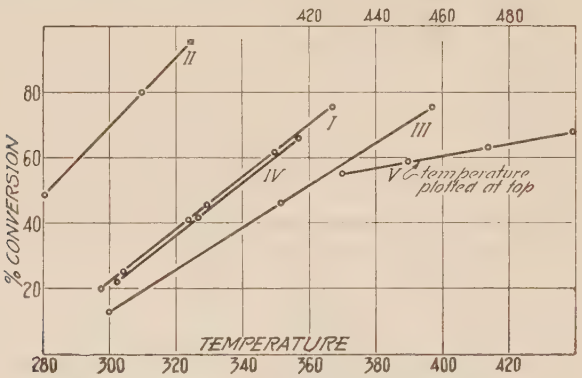

FIG. 4

Reaction velocities on supported catalysts. Curve I-Catalyst I with rate of flow 35 ccs; Curve II-Catalyst II with rate of flow 35 ccs; Curve III-Catalyst I with rate of flow 49 ccs; Curve IV-Catalyst II with rate of flow 350 ccs. Curve V-Catalyst II with rate of flow 23 ccs.

Discussion of Results on Supported Catalysts.—From a comparison of curves 1 and 4 in Fig. 4 it is apparent that the gas mixture may be passed nearly ten times as rapidly over Catalyst II as over I with the same conversion. This is interpreted to mean that the presence of 10% thoria has increased the efficiency of the nickel ten times. It is clear that the increased adsorptions of the reacting gases by the promoted catalyst will not account for the ten fold increase in activity shown by this catalyst, on any basis of quantitative extension of surface alone. Instead of an increase of 900% as would be demanded by such a theory we find actually much less. Upon extrapolation of the curves shown in Fig. 3 it appears that, at 360°, where reaction is 70% complete, the increase in hydrogen adsorption is only about 24% and that of carbon dioxide only about 48%. These facts argue that the change in surface in the case of supported promoted catalysts must be largely qualitative in character.

The possibility of explaining promoter action on a basis of a change in the ratio in which the reacting gases are adsorbed seems, also, unlikely. For, although the value of the ratio CO_2/H_2 appears larger for Catalyst I than for

TABLE II

Adsorptions on Catalyst III (Nickel alone)
Wt. of nickel = 37.98 gms; Density 8.802

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm. 0°	110°	218°	Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm. 0°	110°	218°
N_2	27.7	19.55	15.45			
H_2	52.8	50.55		25.1	31.0	
CO_2	43.15	28.9	25.3	15.45	9.35	9.85
$H_2 = 6$ / $CO_2 = 1$	52.85			25.2		
After heating to 400° C. for 1 hour.						
N_2	27.1	19.35	15.4			
H_2	37.05	33.9	28.1	9.95	14.55	12.7
CO_2	34.15	22.9	20.4	7.05	3.55	5.0
$H_2 = 6$ / $CO_2 = 1$	38.5			11.4		
Percentage decrease in adsorptions due to heat treatment.						
H_2				60.4	53.1	
CO_2				54.4	62.0	49.2
$H_2 = 6$ / $CO_2 = 1$				54.8		

Adsorptions on Catalyst V (nickel plus 10% thoria)
Wt. of catalyst = 20.42 gms; Density = 8.899

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm. 0°	110°	218°	Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm. 0°	110°	218°
N_2	32.2	22.2	17.4			
H_2	58.25	53.45		26.05	31.25	
CO_2	67.9	44.45	33.65	35.7	22.25	16.25
$H_2 = 6$ / $CO_2 = 1$	61.5			29.3		
After heating to 400°C. for 1 hour.						
N_2	32.05	22.2	17.4			
H_2	45.9	38.75	34.4	13.85	16.55	17.0
CO_2	62.15	40.9	30.85	30.1	18.7	13.45
$H_2 = 6$ / $CO_2 = 1$	52.75			20.7		
Percentage decrease in adsorption due to heat treatment.						
H_2				46.8	47.0	
CO_2				15.7	16.0	17.2
$H_2 = 6$ / $CO_2 = 1$				29.4		

Comparisons of adsorptions on Catalysts III and V.

Catalyst	Gas	Vol. of gas N. T. P. adsorbed per vol. of catalyst at t°, 760 mm. 0°	110°	218°	After heating to 400°C. for 1 hour Vol. gas N. T. P. adsorbed per vol. of catalyst at t°, 760 mm. 0°	110°	218°
V	H_2	11.35	13.6		6.05	7.2	7.4
III	H_2	5.8	7.2		2.3	3.35	2.95
Increase		5.55	6.4		3.75	3.85	4.45
Percentage inc.		95.7	88.9		163.0	114.9	150.9
V	CO_2	15.55	9.7	7.1	13.1	8.15	5.85
III	CO_2	3.6	2.15	2.3	1.65	.8	1.15
Increase		11.95	7.55	4.8	11.45	7.35	4.7
Percentage inc.		332.0	351.2	208.7	694.0	906.3	408.7
V	$H_2 = 6$ / $CO_2 = 1$	12.75			9.0		
III	$H_2 = 6$ / $CO_2 = 1$	5.85			2.65		
Increase		6.90			6.35		
Percentage inc.		117.95			239.6		
V Ratio $\frac{CO_2}{H_2}$		1.37	.71		2.17	1.13	
III " "		.62	.30		.72	.24	

Catalyst II at lower temperatures, the difference between these ratios decreases as the temperature increases and, at 285°, where the reaction is still slow, this ratio is practically the same for both catalysts. Therefore, it appears impossible to explain the action of the promoter either by a quantitative extension of surface, or by a change in the relative concentrations of the adsorbed reactants. It seems most probable, however, that the surface of the promoted catalyst is such that it holds adsorbed in a reactive condition a larger fraction of the total amount of gas adsorbed than does the unpromoted catalyst.

If the whole adsorbing surface of the promoted catalyst were actually active catalytically, it is evident that not more than 10 per cent of the unpromoted catalyst surface could possibly be active. Actually the percentage of active surface must be much smaller than this.

Unsupported Catalysts

Adsorption Measurements on Unsupported Catalysts.—In order to prepare unsupported catalysts of high activity, reduction was carried out at as low a temperature as was deemed possible, namely 250°. This procedure had the advantage of making the pure nickel catalyst, used as a basis of comparison, as active as possible, but the disadvantage of making entirely consistent adsorption measurements impossible. Some irregularities were anticipated in working with such active catalysts produced by low temperature reduction, but it is believed that these are small enough as compared to the effects observed to render the conclusions valid. Hydrogen values at 110° and 218° are obviously increased by a slow reduction still occurring at these temperatures. Carbon dioxide values are also large at 218° probably because of a tendency toward carbonate formation at this temperature. However, all values presented are the averages of reproducible check determinations.

In Table II adsorption measurements on Catalyst III, composed of nickel alone, and on Catalyst V composed of nickel plus 10% thoria are given, both before and after the standard heat treatment of 1 hour at 400°. The values for hydrogen adsorption at 0° are somewhat higher than those obtained by either Gauger[1] or Burns[2] for nickel reduced at 300°.

The effect of heat treatment on Catalyst III has been to decrease the adsorption of hydrogen, carbon dioxide and the reaction mixture of these gases about 55%. Catalyst V shows as a result of the heat treatment a reduction in hydrogen adsorption amounting to 47%, in carbon dioxide of only about 16% and in the adsorption of the mixture of an intermediate value of 29%.

From a comparison of the adsorptions of the two catalysts under investigation, the wide difference between the increases in the adsorptions of the two reacting gases on the promoted catalyst is at once apparent. An increase of about 92% for hydrogen but of nearly 342% for carbon dioxide occurs on the promoted catalyst in the temperature range 0°–110°. After the heat treat-

[1] Gauger and Taylor: loc. cit.

[2] Taylor and Burns: J. Am. Chem., **43**, 1273 (1921).

ment the values for hydrogen become about 139% and those for carbon dioxide average 800% over the same temperature range. The promoted catalyst thus shows a greater resistance to heating than does nickel alone. The promoter evidently acts as a support. However, the further function of the thoria in selectively adsorbing carbon dioxide here becomes apparent. The relatively larger adsorptions of carbon dioxide by the promoted catalyst become still larger after heating. The actual increase in ccs. of carbon dioxide adsorbed by Catalyst V as compared to Catalyst III remains practically the same after the heat treatment, while there is a considerable decrease in the corresponding hydrogen values. This means that the relation between the CO_2/H_2 ratios on Catalysts III and V becomes considerably changed due to heating. Between 0° and 110° these ratios are about 1:2 before heating but, afterwards, they are nearer as 1:4. The adsorptions of the reaction mixture show about the same effect. In the case of Catalyst III the adsorption of hydrogen and that of the mixture have the same value. After heat treatment there is a relatively larger adsorption of the mixture than of hydrogen. This relative decrease in hydrogen adsorption may be attributed to a qualitative change in surface due to sintering which has rendered some of the surface formerly capable of adsorbing hydrogen now capable only of holding carbon dioxide. On Catalyst V the adsorption of the mixture is larger than that of hydrogen alone and increasingly so after heating. This must be attributed in part to a specific action on the part of thoria in adsorbing carbon dioxide due perhaps to a tendency for carbonate formation.

In connection with the adsorption of the gaseous mixture it is of interest to note that Hurst and Rideal[1] found for a mixture of carbon monoxide and hydrogen on copper and copper plus palladium surfaces, that the volume of the mixture adsorbed was much less than would be calculated from the adsorption of the two gases separately. This phenomenon is explained by them, on the basis of the polarity of the carbon monoxide molecule. Since carbon dioxide is a non-polar gas, however, we should expect to find more or less additive relations or simple replacements involved in the behavior of mixtures of carbon dioxide and hydrogen on finely divided metal surfaces. Such seems to be the case with nickel.

Reaction Velocity Measurements on Unsupported Catalysts.—Three unsupported catalysts were investigated: Catalyst III composed of nickel alone, weight 4.7961 grams; Catalyst IV composed of nickel plus 2% thoria, weight 4.5565 grams; and Catalyst V composed of nickel plus 10% thoria, weight 4.8059 grams. The behavior of these catalysts both before and after heat treatment is shown in Fig. 5. The results are treated in the same manner as were those of the supported catalysts. The rate of gas flow is in all cases the same, 49 ccs. per minute.

When compared with the supported catalysts the difference in the temperature range at which comparable conversions are occurring is apparent. The difference in the temperature of reduction of these two types of catalysts is

[1] Hurst and Rideal: J. Chem. Soc., **125**, 694 (1924).

probably one of the chief factors causing this phenomenon. Taking comparable conditions, we have 50% conversion shown by Catalyst IV at 196°, by Catalyst V at 200°, by Catalyst III at 223°, but by Catalyst I at 358°. The first in order were reduced at 250° while the last was reduced at 350°. One of the effects of the standard heat treatment has been to raise considerably the temperature at which equivalent conversion occurs.

The slopes of the reaction velocity curves are somewhat steeper for the unsupported catalysts and steepest for Catalyst IV which shows the greatest promotion at the lowest temperature. This is more strikingly illustrated by Curve 5 in Fig. 4 which shows the course of the reaction at 430-500°.

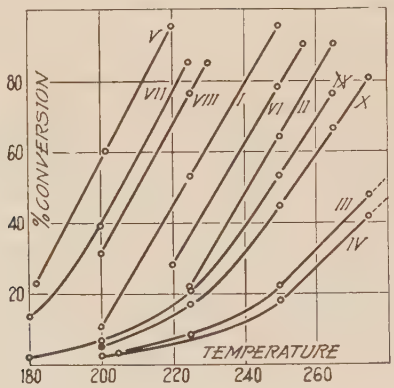

FIG. 5

Reaction velocities on unsupported catalysts. Rate of flow 49 ccs. Catalyst III: Curve I initial rate; Curve II rate after 25 hours' run; Curve III rate after 1 hour at 400°; Curve IV rate after 2 hours at 400°. Catalyst IV; Curve V initial rate; Curve VI rate after 1 hour at 400°. Catalyst V: Curve VII initial rate; Curve VIII rate after 25 hours' run; Curve IX rate after 1 hour at 400°; Curve X rate after 2 hours at 400°.

It will be noted that for Catalysts III and V curves are shown designated as "initial rate" and "rate after 25 hours use." The "initial rate" curves represent the activity on the catalyst as determined by the first 4-5 hours run. Catalyst III showed a continuous decrease in activity with use, and after 25 hours, a slow depreciation still occurred. At the end of this interval this catalyst showed its initial activity 18° higher than at the beginning. Catalyst V after 25 hours use had acquired a steady rate, with a change in initial reaction temperature of only 5°. Catalyst IV maintained its initial activity with continued use. This catalyst, also, contained nearer the optimum amount of thoria as determined by Medsforth than did V. These facts would indicate that the optimum amount of promoter not only gives the greatest activity but also creates the surface of greatest permanence and durability. The marked depreciation which Catalyst III suffered with use is in all probability due to the exothermicity of the reaction (40,500 cals.) occurring on the active surface of the catalyst. The heat of reaction is great enough to cause a slow sintering of this surface and the consequent loss in activity. That the pro-

moted catalysts did not depreciate thus, is an indication as to the function of the thoria as a support material.

At 50% conversion Catalyst IV has the same activity 27° lower than Catalyst III while Catalyst V is 17° lower than nickel alone. If the rates after 25 hours use were to be compared, the promoted catalysts would appear somewhat more favorably still. Of the promoted catalysts we are more interested in V because of the adsorption measurements made upon it, and also because it contains the same ratio of nickel to thoria as did Catalyst II. Catalyst V has the same activity as Catalyst III at a temperature 17° lower. To obtain an idea of the relative activities of these two catalysts we will assume that the ratio of the temperature coefficients on Catalysts II and V is also the ratio between the increases in activity which these catalysts show with rising temperature. Since it was found that a 55° difference in temperature between Catalysts I and II corresponded to a ten-fold increase in activity for II, and since the slopes of the curves for Catalysts II and V are 1:1.9, we find that a 17° difference in temperature between Catalysts III and V should correspond to approximately a six-fold increase in activity for V. By the same reasoning Catalyst IV would show about a 9.5-fold increase in activity over Catalyst III.

As a result of the standard heat treatment a loss in activity at 50% conversion equal to 54° occurs with Catalyst III while under similar treatment Catalyst V suffers a loss equivalent to but 42°. This may be interpreted to mean that Catalyst III showed approximately a 28.5% larger decrease in activity than did Catalyst V.

Physical Effects of Heat Treatment.—When pure nickel oxides are reduced by hydrogen the resulting product is usually a dense, dull black powder, or a substance easily reducible to powder form. If irreducible impurities such as oxides are present even in small amounts, a jet black powder of a much less apparent density results. When a promoter of the thoria type is present it acts as an impurity to prevent sintering and, therefore, to maintain a greater surface.

As a result of work done in 1899 on the occlusion of hydrogen by metallic cobalt and other metals including nickel, Baxter[1] showed that the adsorptive capacity of metals for hydrogen depended upon the temperature at which their oxides were reduced or the temperature to which they were subsequently heated. He also observed that, "Metal reduced from the impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided tendency to cling together. This sintering can be nothing more or less than incipient fusion. When the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect." The results of the present work are in agreement with these ideas.

At a temperature as low as 250° the volume of the pure nickel catalyst was only about three-quarters of that of the original oxide before reduction,

[1] Baxter: Am. Chem. J., **22**, 351 (1899).

while the promoted catalyst reduced at the same temperature showed little shrinkage. Some data on the apparent densities of the unsupported catalysts are given in the following table.

Catalyst	Apparent Density	Apparent Volume
III	1.44	0.69
III (heat treated)	1.81	0.55
V	0.90	1.11
V (heat treated)	1.20	0.83

The effect of a second similar heating on catalysts used for reaction velocity measurements produced much less effect. This is evident from the relation of the positions of curves 9 and 10, also 3 and 4 in Fig. 5.

It appears evident from the preceding data and from the adsorption and reaction velocity measurements on unsupported catalysts before and after heat treatment that the nature, extent, and catalytic activity of a surface are dependent upon (a) the purity of the metal, that is, the presence or absence of foreign substances which may act as promoters. (b) the highest temperature at which the surface has been allowed to equilibrate itself. These conclusions are in line with Baxter's work and that of Pease[1] with copper.

Discussion of Results on Unsupported Catalysts.—The proportionately larger increases in the adsorption of the reacting gases on the promoted, unsupported catalyst will more nearly account for the increase in activity found than was the case with the supported nickel. Catalyst V showed only a six-fold increase in reaction velocity over that of Catalyst III, but an average increase in hydrogen adsorption of some 92% and in carbon dioxide adsorption of some 342% occurred in the temperature range 0°-110°. A quantitative extension of surface must therefore in part account for the increased activity. The thoria here is acting partly as a support. This view is substantiated first by the increased apparent volume of the catalyst and second by the longer time necessary to obtain equivalent reduction, e.g. 384 hours for Catalyst V as compared to 192 hours for Catalyst III. That supported nickel cannot be reduced at as low a temperature as the unsupported material is well known.

Catalyst V did not contain the optimum concentration of thoria although the ratio of thoria to nickel was theoretically the same as in Catalyst II. Catalyst IV with only 2% thoria was more active. Aside from a possible blanketing effect[2] it is believed that thoria, in amounts above the optimum, causes a retardation in the reaction due to a disproportionately large adsorption of carbon dioxide. The CO_2/H_2 ratio on Catalyst V is more than twice that on Catalyst III and after heat treatment becomes more nearly four times as much. The hydrogen adsorption is dependent upon the extent of surface, whereas the carbon dioxide is being adsorbed in two ways, first by the nickel surface and second specifically by the thoria. This latter type of adsorption is apparently little altered by heat. The effect of heat treatment on the promoted nickel is, therefore, two-fold, first a disappearance of surface due to

[1] Pease: J. Am. Chem. Soc., **45**, 2296 (1923).

[2] Armstrong and Hilditch: loc. cit.

sintering, and second an unfavorable change of the CO_2/H_2 ratio. These two factors would make high temperatures especially disastrous to nickel promoted by thoria were it not for the action of the thoria in decreasing materially the amount of sintering.

As was previously noted, the standard heat treatment has caused approximately a 28.5% larger decrease in the activity of Catalyst III than it has in that of Catalyst V. The decrease in hydrogen adsorption at 0° due to this heat treatment was 60.4% on Catalyst III and 46.8% on Catalyst V. This gives approximately a 29% larger decrease for hydrogen adsorption for Catalyst III than for V. This points to a dependence of the reaction on the hydrogen adsorption. It is also of interest to note that the ratio of the increase in density of Catalyst III over V due to heating is 1.23 while the ratio of the displacements of the reaction velocity curves due to heating is 1.28 at 50% conversion.

Conclusions

It is believed that the results obtained from the work presented in this paper can best be explained in terms of the following theory.

The nature of the surface of a nickel catalyst produced by the reduction of the oxide is determined (a) by the nature and amount of foreign substances present, and (b) by the temperature of reduction. The most active catalyst imaginable would be one consisting of single atoms of the metal sufficiently isolated from each other so that all their valence forces would be available for adsorbing the reactants, and in certain cases the resultants. A most inactive catalyst, on the other hand, would be one whose atoms were regularly arranged in their stable crystal lattice with the consequent almost complete mutual saturation of valence forces. This latter type is easily realizable with metals in the massive state, when adsorptions are immeasurably small and catalytic power negligible. The former extreme type would not be experimentally realizable nor would it be an effective catalyst for many reactions because it would enter into true chemical combination with adsorbates. Catalysts actually realizable will have their atoms only partly unsaturated and will, therefore, hold the adsorbate with only part of the whole valence force. It, therefore, follows that the greater the irregularity of the metal atoms, e.g. the further they are removed from their regular crystal lattice the greater the force by which they can hold molecules by adsorption. The force which a catalytic surface exerts in adsorption will be equal to the sum of the total valence forces of the atoms concerned multiplied by a factor expressing the average degree of unsaturation of the component atoms.

The lower the temperatures of reduction the more unsaturated the resultant metal atoms. Other things equal the lowest temperature at which reduction will proceed will give the greatest realizable unsaturation, because, here, mobility of the metal atoms is least and, therefore, their tendency to mutual saturation a minimum. With rising temperature, a surface adjusts itself by an irreversible mutual saturation, or as is usually said "sinters." The function of a promoter of the thoria type is to prevent this saturation or

sintering. The presence of the saturated molecules of thoria, which are more or less neutral electrically and which act as insulators between the charged metal atoms, prevent coalescence and consequent saturation. Foreign oxides which undergo reduction (preliminary work on mixtures of nickel and copper showed no promoter action) are not effective as promoters as they do not prevent saturation and may even assist it. The promoter, therefore, makes possible the production of a surface containing atoms of a more unsaturated character than it is possible to produce from the pure metal oxide under similar conditions of reduction. The efficiency of a promoter in preventing coalescence must, therefore, depend upon (a) the amount present (b) its distribution (c) its chemical and consequent electrical properties.

It is believed that the promoting action of thoria on nickel supported by pumice is largely due to such an increase in the unsaturation or activity of the surface. This increase in the activity of the surface of the promoted catalyst manifests itself (a) by a disproportionately large increase in reaction velocity as compared to the increase in extent of surface (b) by manifesting an equivalent activity at a lower temperature (c) by showing the higher temperature coefficient of the surface reaction. Other factors also become of importance in the case of unsupported nickel promoted by thoria. Here, the thoria acts also as a support to increase the extent of surface. This increase in extent of surface on the part of the unsupported promoted catalyst is shown (a) by its increased adsorption values (b) by the greater apparent volume of the catalyst (c) by the increased time necessary for reduction.

That the optimum ratio of thoria to nickel should be less for the unsupported nickel catalyst even though the thoria acts as a support is explained by the fact that much of the nickel present is also acting as a support and has little or no catalytic significance. The specific action of thoria in adsorbing carbon dioxide, aside from considerations of surface as shown by the effects of heat treatments, demonstrates the influence which the promoter may exert on the ratio in which the reacting gases are adsorbed. The behavior of the unsupported catalysts after heat treatment indicates that this last factor has become a retarding influence but is still more than compensated by the other factors still operating in a positive direction. Substances which cause the reactants to be adsorbed in an unfavorable ratio or lead to stable compound formation will act as poisons rather than promoters.

Summary

1. The reaction between carbon dioxide and hydrogen to form methane and water is a surface reaction, markedly so at low temperatures, and strongly affected by the adsorbing power for the reactants, of the surface catalyzing this reaction.

2. The activity of nickel alone, supported or unsupported, is dependent mainly upon the temperature at which it is reduced. Other things being equal, the lower the temperature of reduction the greater is the number of highly unsaturated nickel atoms which can exist per volume of catalyst.

These atoms are assumed mainly responsible for catalytic activity. A surface stable at the temperature of reduction or lower is profoundly modified when subjected to higher temperatures. The change consists in the coalescence of these unsaturated atoms due to valence force attraction, when their mobilities are increased with temperature, and their consequent saturation, whole of partial, and loss of effective adsorption por.

3. The primary function of the promoter, thoria, with supported nickel is to make possible, through the creation of thoria-nickel interfaces, the existence of a greater number of nickel atoms of a more highly unsaturated charr acter per unit of catalyst than can exist in nickel alone, reduced under similar conditions.

4. Thoria may function in at least three ways in promoting catalysts of unsupported nickel (a) by the creation of a more active surface through the interface mechanism as in the case of supported catalysts (b) by an increase in the extent of surface in as much as the promoter acts as a support (c) by a favorable alteration in the ratio in which the reacting substances and possibly the products of reaction are adsorbed. A catalyst of maximum reactivity for a given reaction will, therefore, be produced when the nature, amount, and distribution of the promoter is such as to give the proper balance between these effects.

5. These conclusions have been based upon the results of both adsorption and reaction velocity measurements on samples of promoted and unpromoted, supported and unsupported nickel catalysts.

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